Standard Operating Procedure for the Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatography Separation with Speciated Isotope Dilution Mass Spectrometry

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Application:

Applicable Matrices: This method may be used to determine methyl mercury (MeHg) concentrations in filtered or unfiltered water samples.

Minimum Reporting Limit: ≤0.040 ng/L (nanograms per liter).

Dynamic Range: This method is designed for the measurement of MeHg in the range of 0.040 - 5 ng/L. The upper range may be extended to higher levels by distilling a smaller sample volume or ethylating a smaller aliquot of the distillate.

Method Summary: Water samples are spiked with isotopically enriched standard and distilled to remove potential interferences. The pH of the distillate is adjusted to 4.9 using acetate buffer. The distillate is then ethylated using sodium tetraethyl borate ($NaTEB_4$) and allowed to react for 15 minutes. Following reaction with NaTEB the distillate is purged with grade 5 Argon gas (Ar) for 20 minutes and the ethylated mercury species are collected on a Carbotrap. The ethylated mercury species are thermally desorbed from the Carbotrap, separated using a gas chromatography (GC) column, reduced and ionized using the ICP-MS, and detected using Speciated Isotope Dilution Mass Spectrometry (SIDMS).

Interferences:

The distillation procedure is intended to eliminate interferences from the water sample during the ethylation and analysis procedure.

Large amounts of water vapor absorbed onto the Carbotraps during bubbling will cause an instrument response in excess of system sensitivity. The response from the water vapor will mask the response from the ethylated mercury species in the sample, resulting in loss of the sample.

Apparatus and instrumentation:

Flow meter(s) equipped with needle valves to maintain a Ar flow of 250 mL/min.

Reaction vessels are 250 mL Erlenmeyer flask with the standard 24/40 tapered neck. A sparging stopper fitted with a special four-way valve is used to close the reaction vessel. The four-way valve allows the sample to react with the ethylating reagent in a closed environment, then to be purged onto the Carbotrap without opening the flask.

The Carbotraps are constructed of a 7 mm quartz tubes, 10 cm long with a constriction at 3 cm from the outlet end; about 0.2 g (3 cm in the tube) of Carbotrap (graphitized carbon black, Supelco 2-0287 or equivalent) is placed in the center and contained by quartz wool plugs at either end. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the sample traps to provide a connection point between the sample trap and the reaction vessel and in the analytical train.

End plugs are created by heating ¼" Teflon tubing and sealing one end by pinching with pliers.

Sample volume is measured with an analytical balance capable of measuring to the nearest 0.1 g.

All-plastic pneumatic fixed-volume and variable pipettes in the range of 5 μL to 5 mL.

A simple contact switch, connected to a timer, controls the analytical system. The timer is connected to a transformer, which is then connected to a Nichrome wire coil wrapped to fit around the Carbotrap. The Carbotrap is heated to 250^{o}C with a ramp time of 30 seconds. The detector analog output is captured by PeakSimple or similar chromatographic software.

The gas chromatographic column is a 4 mm i.d., 6 mm o.d., glass column 50cm long and filled with Chromosorb WAW-DMSC 60/80 mesh (Supelco 2-0152) enclosed in a glass sheath 2 cm in diameter and 25 cm long. This column is housed in a cylindrical oven connected to a transformer, which supplies a constant voltage to maintain a temperature of 95 +/- 5^{o}C.

Reagents and Standards:

Reagents: All reagents and/or dry chemicals used to make reagents must be of the highest purity available from the vendor and shown to be low in mercury. Upon receipt at the laboratory, containers will be marked with the date of receipt and stored in the appropriate areas. When reagents are mixed for use in this method, the person who mixes them will initial and date the reagent container.

Reagent water: Ultra pure reagent grade water shown to be > 18 MΩ starting from pre-purified source (distilled, RO, etc.). The water is delivered through a 0.2 uM filter. All water is obtained from a Millipore Academic water purification system.

Acetate buffer: Dispense approximately 50 mL of reagent water and 11.8 mL of glacial acetic acid into a 125 mL mercury clean Teflon bottle. Add 27.2 g reagent grade sodium acetate to this solution and dilute to mark with reagent grade water. Place bottle in UV cabinet to photo degrade any methyl mercury. This solution has an indefinite shelf life.

Ethylating Reagent: Sodium Tetraethyl Borate ($NaTEB_4$) is purchased in 1 gram (Strem 11-0575) sealed bottles and kept in the freezer. In a 125 mL Teflon bottle, dissolve 2 g Potassium Hydroxide (KOH) in 100 mL of reagent grade water and chill to 0^{o}C. When the KOH solution becomes slush, remove a bottle of $NaTEB_4$ from the freezer, remove the top of the bottle, and empty the contents into the KOH solution, recap and shake to dissolve.. Immediately, the 1% NaTEB4 in 2% KOH solution is divided equally into 9 clean 15 mL Teflon vials that are capped and frozen. The date prepared is written on the vial rack. This solution should be kept frozen and made fresh every 2 weeks. Never use $NaTEB_4$ solid or solutions that are yellow in color. *Note: $NaTEB_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaTEB_4$ use should take place in a high-volume fume hood. To discard unused portions of ethylating reagent, empty bottles into a large beaker of 6N hydrochloric acid (HCl) inside a high volume fume hood. Place beaker on a hotplate and boil down to half-volume then discard the remaining solution as an acid waste. Triethylboron will boil off into the air where it is oxidized to harmless boric acid.*

Argon (Ar): Ultra high purity grade 5.0 Ar is used as to bubble the Hg species onto the Carbotraps, and as the carrier gas in the analytical system. The Ar is first passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

25% $CuSO_4$ solution: In a 500 ml Teflon bottle, add 125 g $CuSO_4$ and bring up to 500 ml volume with reagent water. Shake well until all solids dissolve.

Standards

Upon receipt at the laboratory or on the day of preparation, standards should be labeled with the date received or made and the initials of the person preparing them. Highly concentrated stock solutions should be stored away from the main working areas to prevent contamination of the clean lab. Working standards and (if necessary) subsequent sub-stock dilutions should be made in a class A volumetric flask in a matrix of reagent grade water at a 2% and 0.2% concentration of glacial acetic acid and hydrochloric acid, respectively. This solution should be transferred to a Teflon bottle designated specifically for mercury standards, stored in an amber bag at 4^{o} C, and remade every 6 months. All standards must be assigned a unique letter-number-letter identification code and be entered into the laboratory database system. For working solutions of native MeHg, allow the solution to equilibrate for at least 24 hours and then determine the concentration by analysis via cold vapor atomic fluorescence spectrometry as follows:

1. Mass of mercury in the MeHg standard: To four 15 ml Teflon vials, add 8.0 ml of reagent grade water, 1.000 ml of the MeHg working standard, and 1.0 ml of BrCl.

2. Blank contribution of mercury: To four 15 ml Teflon vials, add 9.0 ml of reagent grade water and 1.0 ml of BrCl.

3. Store the vials in a rack, seal in a bag, and heat in an oven to 50^{o} C for eight hours.

4. Analyze the contents of the eight Teflon vials by EPA method 1631.

5. Analyze four 1.000 ml additions of the MeHg working standard to determine the $SnCl_2$ reducible fraction of Hg^{II}

6. Subtract the average blank mercury mass and the $SnCl_2$ reducible fraction of Hg^{II} from the total mercury mass determined MeHg working standard to determine the actual MeHg mass in the vials and subsequent concentration.

Sample Preservative, Containers, and Holding Times:

Samples are preserved by acidifying to 1% HCl with mercury clean HCl. After acidification samples should be kept in the dark to prevent photodegradation of methylmercury.

Sample containers will consist of Teflon bottles cleaned at the laboratory. New Teflon bottles are rinsed with tap water, and cleaned by immersing in 4 N trace pure HCl heated to 65^{o}C for at least 48 hour. Immediately following removal from the bath, the bottles are immersed in fresh reagent grade water and rinsed at least 3 times with reagent grade water. Following the rinsing step, each bottle is filled to 25% with 1% trace pure HCl and capped. The exterior of the bottles is allowed to air dry under a mercury-free class 100 laminar flow hood. Dry equipment is double bagged in new zip-type bags with the unique identifier and date cleaned written on the outer bag. After the initial 48 hr. cleaning, only a 24 hr. soak is required.

Properly preserved samples may be held for 6 months at the laboratory.

Distillates should be analyzed within 48 hours of distillation.

Safety Issues: Before beginning any of the procedures involved in this method, each individual must read and sign the Chemical Hygiene Plan developed for the lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets for that chemical – all of which are located in the laboratory.

Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Due to the toxicological and physical properties of Hg, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of vinyl gloves and high volume hoods when preparing standards.

Strong acid solutions are employed in the cleaning of equipment and preparation of reagents. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant clothing and the utilization of high volume fume hoods.

$NaTEB_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaTEB_4$ use should take place in a high volume fume hood. To discard unused portions of ethylating reagent, in a high volume fume hood empty bottles into a large beaker of 6N hydrochloric acid (HCl). Place beaker on a hotplate and boil down to ½ volume then discard remaining solution as an acid waste. Triethylboron will bubble off to the air where it is oxidized to harmless boric acid.

General Description:

The procedure for conducting methyl mercury analysis using isotope dilution differs from isotopic analysis with the addition of the internal isotope working standard. This adds one additional round of analysis after the ethylation blanks, to determine the concentration of the isotope working standard. This method may also be used for isotopic tracer analysis, as long as the isotope of the working standard or the ambient reference isotopes were not used as a tracer. The concentration of the samples is determined using the following equation:

$$\text{ng per sample distillate} = R_S * \text{ng ID} * R_A / M_A$$

ng ID= nanograms of ID spike per distillate
R_S = the peak area ratio 202/199 in the sample
R_A= the mass bias determined from the standard "curve"
M_A= the mass percent of the ambient isotope

The ng ID is determined from the isotope standard "curve" using the following equation:

ng ID = (ng std) * (atomic weight spike)/(atomic weight std) * [(R* atomic %199 std) - atomic %202 std/[(atomic %202 spike - (R*atomic %199 spike)

R= the peak area ratio (202/199)

The concentrations of the samples are determined by dividing the blank corrected nanograms per sample distillate divided by the original volume distilled.

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Detailed procedure:

Helpful hints:

When working with detection limits in the parts per trillion range, protection of these samples from contamination cannot be over emphasized. The greatest difficulty in low level MeHg analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout the bottle preparation, collection, and distillation procedures to avoid contamination.

Extreme caution should be exercised during bubbler rinsing to avoid residual water in the four-way valve. If water is apparent in the valve, use a cotton swab to remove it before allowing flow through the Carbotrap.

Distillation Procedure

A typical distillation contains 32 samples, four blanks, and two duplicate spikes. In small sample sets (< 16), four method blanks, and one duplicate spike should be included in each run.

1. Throughout the distillation process, it is important for the analyst to develop and maintain a structured and organized system. Each distillation and receiving vessel has a unique identification code etched onto the wall. The corresponding vials must be appropriately linked to each other, as well as back to the original sample. Good record keeping must occur not only throughout the distillation process, but must be similarly well documented in the Excel data sheet. See Appendix 1 for more details.

   Example: Sample Id → Distillation vial #001 → Receiving vial → #100

   A template of the Excel data sheet can be found at: HG4\hg4data\.

2. Before beginning sample setup, turn on the aluminum block heater so that it can reach temperature while samples are being prepared.

3. Arrange an adequate number of clean Teflon distillation and receiving vials into acrylic sample racks.

4. Weigh approximately 60 grams of sample (or reagent water for method blanks) into each of the distillation vials. Be sure to homogenize the sample by inverting the sample bottle several times before dispensing to the distillation vial. Setup two samples in triplicate for the duplicate spike analysis. Be sure that you record the sample ID, distillation vial ID, distillation vial tare weight, and the sample mass into the appropriate places in the Excel data sheet.

5. To each of the distillation vials, add 1 ml of 25% $CuSO_4$ solution. The method blanks should be acidified with 600 µl of concentrated HCl.

6. Add 100 µl of the working standard to each of the duplicate spike samples.

7. Fit each distillation vial with a combined distillation cap/transfer tube assembly corresponding to the block position to be occupied by that vial (each cap has been engraved with a number between 1 and 40).

8. To each of the receiving vials, add 40 ml of reagent water. Be sure that you record the receiving vial ID and receiving vial tare weight.

9. Fit each receiving vial with a distillation cap corresponding to the rack position to be occupied by that vial (each cap has been engraved with a number between 1 and 40).

10. Place the distillation vials in the bore holes of the preheated (approximately 120º C) aluminum block. Attach an argon gas line to each of the distillation caps and ensure that gas flows through the sample.

11. In an ordered manner, thread the transfer tubes through the Teflon ports in the side of the cooler.

12. In the cooler, attach each transfer tube to the corresponding receiving vial. Ensure that gas flows in the reagent water of the receiving vial.

13. Throughout the distillation, check the temperature of the heating block often. Adjust to maintain a temperature of 121º C (± 5).

14. Check the distillation vials regularly. Samples are finished distilling when approximately 25% of the original sample is left.

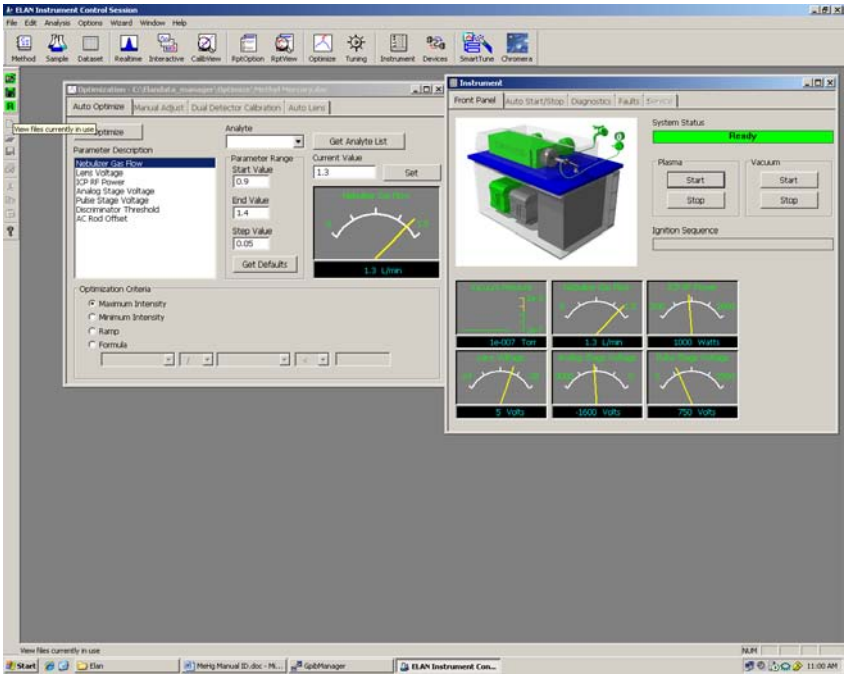
15. Once a sample is finished, disconnect the transfer tube from the receiving vial and the gas line from the distillation cap. Cover the gas inlet port of the distillation cap quickly with a gloved finger to keep the sample in the vial from discharging.

16. Thoroughly rinse the combined distillation cap/transfer tube assembly with copious amounts of reagent water. Place the caps in the laminar flow hood to dry.

17. Once the entire distillation is finished, remove the receiving vials from the cooler and remove the distillation caps. Record the mass of the receiving vial in the Excel data sheet and attach a standard cap.

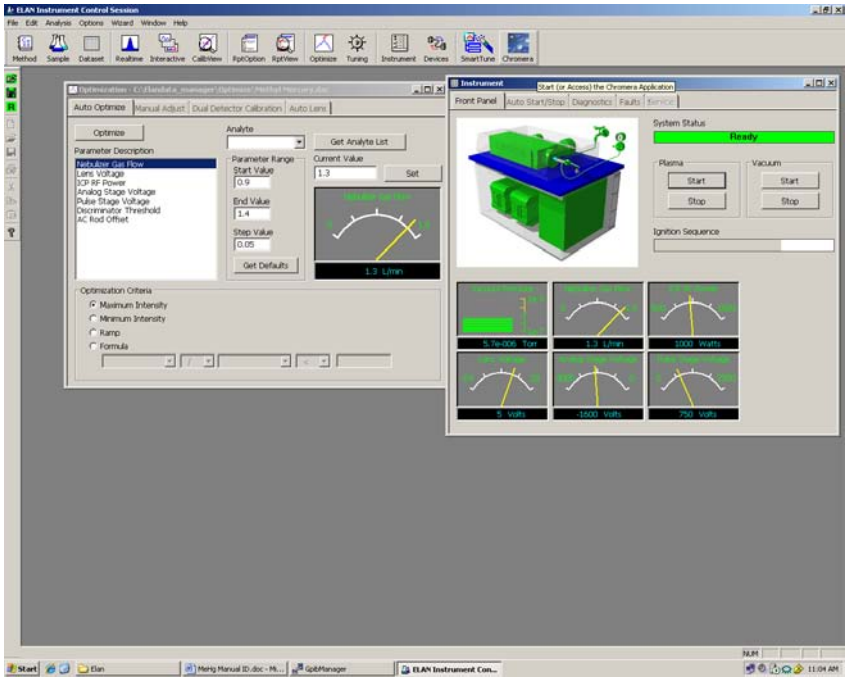
Initial setup and sample analysis:

Log onto the computer. Turn on the recirculator switch on the opposite side of the lab door jam from the light switch. Start the Elan software by double clicking the desktop shortcut labeled **Elan**.

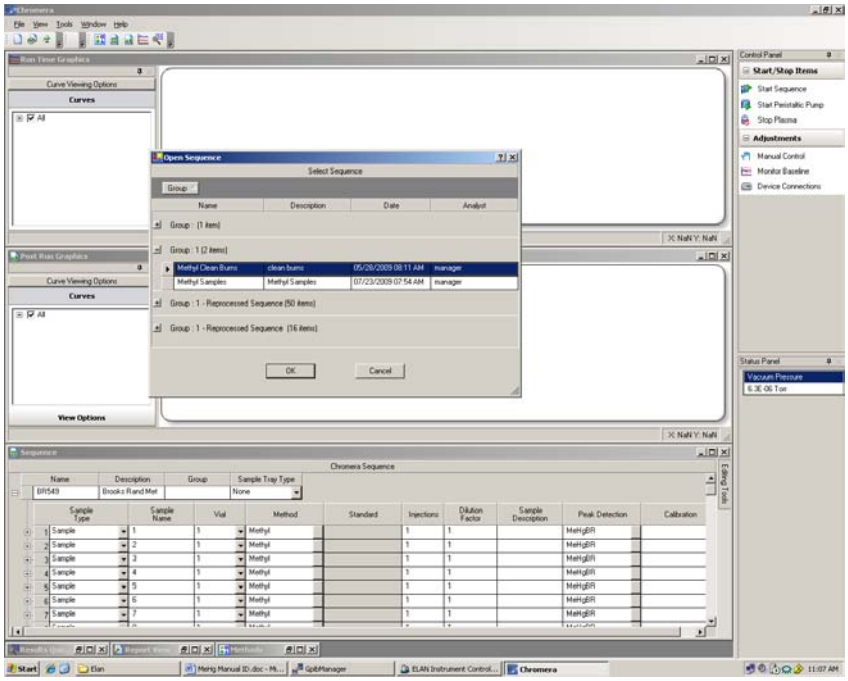


Verify that the methyl mercury workspace is open by clicking the **R** button in the upper left corner of the workspace and that the **Methyl Mercury.**dac file has been loaded. Verify that the ICP-MS is ready by viewing the instrument window. Verify that the external mass flow controller is reading 30.0 ml/min. Start the plasma by clicking the **Start Plasma** button in the instrument window.

Check the temperature of the GC column oven to verify it is at 95^0 C.

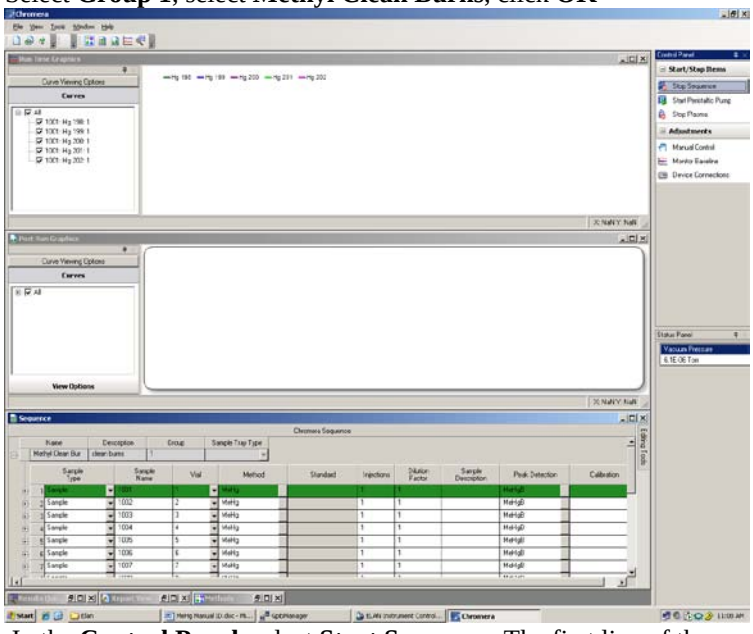


Launch **Chromera** by clicking the icon at the far right of the toolbar column.



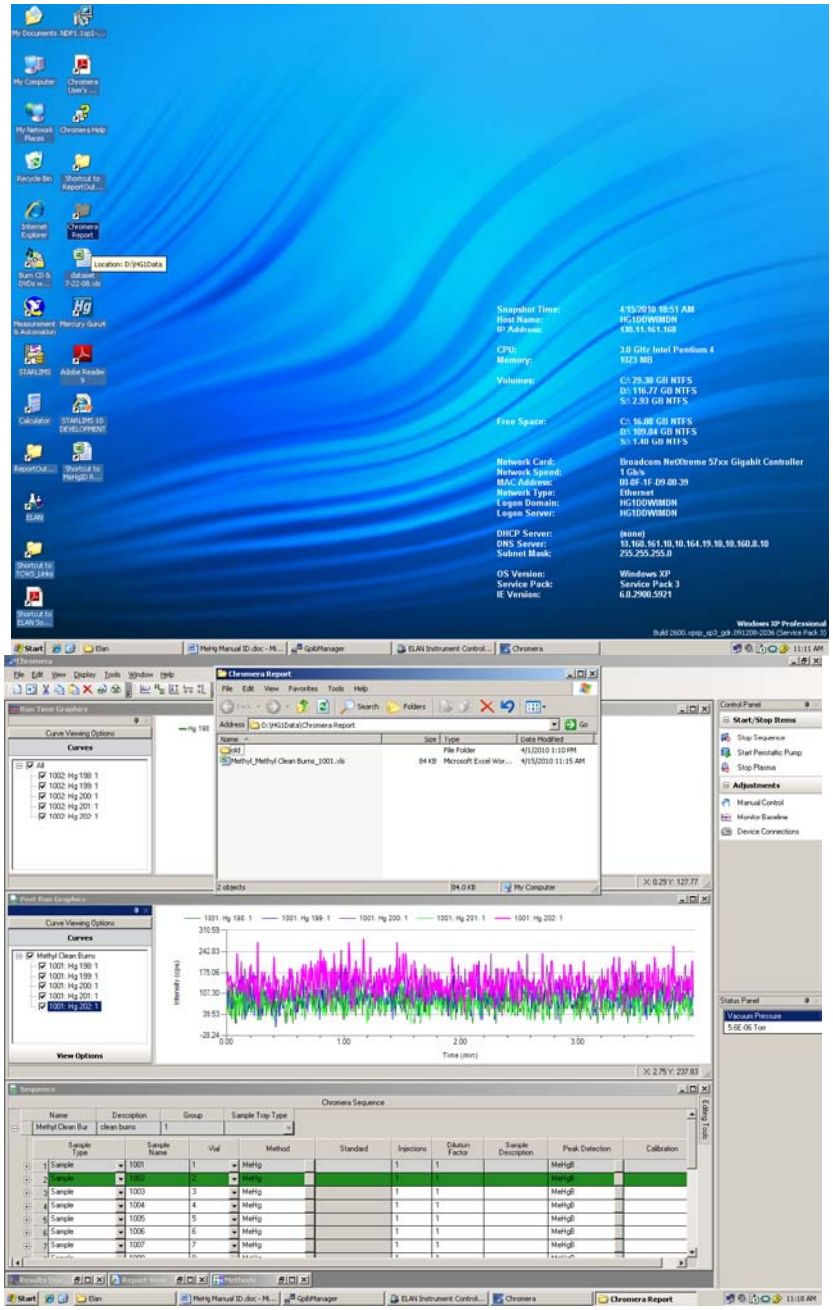
Select the **Sequence** window, then **Open Sequence** from the **File** menu.

Select **Group 1**, select **Methyl Clean Burns**, click **OK**



In the **Control Panel**, select **Start Sequence**. The first line of the sequence should turn green.

Remove the plugs from the ends of the first trap and place it into the analytical train by threading it, with the id number upstream, through the center of the Nichrome wire coil. Center the Nichrome wire over the graphitized carbon black on the Carbotrap and press Program, 1, On, on the Chrontrol. The program will start after a 30 second delay.



After the clean burn is completed, the second line the sequence will be highlighted green and the first clean burn report file will be sent to the **Chromera Report** folder. After the 4-minute cycle is complete, repeat the steps in 1.4.4.3 for each of the remaining traps.

You need to have 5 traps burned before step 1.4.9 is complete. You have 10 traps and five bubblers. Sample reaction time is 15 minutes and bubbling time is 20 minutes -- the burning (analyzing) of 5 traps takes 25 minutes, you will be reacting, bubbling, and drying a round of samples while burning the previous round. This is the cycle you will follow throughout the day.

Thoroughly rinse the bubblers and sparging stoppers with reagent grade water.

Dispense approximately 100 mL of reagent grade water into each of the bubblers.

Pipette 200, 100, 50, 25 and 10 µl of working standard into bubblers 1,2,3,4 and 5 respectively. These bubblers represent your standard curve.

Pipette 200 µL of acetate buffer and 100 µL of $NaTEB_4$ to each of the bubblers.

> *Note: The $NaTEB_4$ needs to remain at near 0^0 C. It should be removed from the freezer approximately 5 minutes before being added to the bubbler and placed in the dark place to partially thaw.*

Tighten the sparging stoppers, ensure the four-way valve is in the closed position, gently swirl the bubblers, and allow to react for 15 minutes. While the samples are reacting connect the Ar line to the inlet of the stopper to purge the four-way valve of air and residual moisture.

After the reaction time has elapsed, remove the plugs from the ends of the Carbotraps, place them onto the outlet of the bubbler with the id numbers downstream, turn the four-way valve to the open position, and allow to purge for 20 minutes.

After the 20 minute purge, turn the four-way valve to the closed position, remove the Carbotraps from the reaction vessel outlet, remove the Ar line from the inlet of the four way valve, and place the Carbotrap on the end of the Ar line with the id numbers downstream. Allow to dry for 7 minutes.

Thoroughly rinse the reaction vessels and sparging stoppers with reagent grade water.

Dispense approximately 100 mL of reagent grade water into each reaction vessel.

Pipette 200 µL of acetate buffer and 100 µL of $NaTEB_4$ to each of the bubblers. These reaction vessels are your ethylation blanks.

While the ethylation blanks are reacting, remove the Carbotraps from the Ar lines, attach the Ar lines to the inlets of the four-way valves, and cap both ends of the Carbotraps.

Analyze the Carbotraps used to collect the standards by opening and starting the Methyl Sample Sequence.

> Open the sample workbook by logging into HG4 in My Network Places and finding the appropriate file in the Methyl Isotope Folder. Full and empty weights of the To Vials will be recorded on the **Set Up** Worksheet. Peak areas are copied out of the Chromera report files and pasted into the **Peak Area-Curve** Worksheet by selecting Paste Special-Transpose. The cells directly below the area cells convert these values to non-comma delimited. Copy and Paste Values non-comma numbers into the appropriate line of the **Peak Area-Curve** Worksheet.

After the blanks have finished purging, thoroughly rinse the bubblers and sparging stoppers with reagent grade water and setup the ID Standards round. Use an adequate amount of ID standard, usually the same amount that was added to the samples prior to distillation. The amount of ambient standard is usually determined by the midpoint of the standard curve. In this example, that would be 50 µL. Check Standards 1-5 will have varying amounts of ambient standard, but will each contain the same amount of ID standard as the ID standard round.

The table below outlines a typical manual analytical batch.

EB - ethylation blank/bubbler

Round	Reaction vessel 1	Reaction vessel 2	Reaction vessel 3	Reaction vessel 4	Reaction vessel 5
Standards	200 µL	100 µL	50 µL	25 µL	10 µL
Blanks	EB1	EB2	EB3	EB4	EB5
ID Stds	50 µL + 50 µL	50 µL + 50 µL	50 µL + 50 µL	50 µL + 50 µL	50 µL + 50 µL
Blanks	MB1	MB2	MB3	MB4	S1
Samples	S2	S3	S4	CHK1	S5
Samples	S6	S7	S8	S9	S10
Samples	S11	S12	CHK2	S13	S14
Samples	S15	S16	S17	S18	S19
Samples	S20	CHK3	S21	S22	S23
Samples	S24	S25	S26	S27	S28
Samples	CHK4	S29	S30	S31	S32
Samples	S33	S34	S35	S36	CHK5

blank
MB - method blank/distillation blank
CHK - check standard (ID and ambient
S - sample

Calibration and performance documentation: During the analysis run, the analyst must evaluate the calibration data, ethylation blank values, MS/MSD recoveries, and check standard recoveries to ensure acceptance criteria are being met. The spreadsheet created during the distillation of the samples is where this information is recorded.

Performance Criteria:

Mass Bias:

The calibration curve is used to determine the mass bias correction. The average ratio of the five standards is divided by the IUPAC mass ratio, which is 1.77 for 202/199. This value must be within 5% of the expected value for the isotopes of interest.

The %RSD (Standard Deviation/Average) must be less than or equal to 10%.

Reverse ID:

The %RSD (Standard Deviation/Average) of the calculated concentration of the isotope dilution standard must be equal to or less than 10%.

Method Blanks:

The Absolute Detection Limit (three times the standard deviation of the method blank masses) must be less than or equal to 0.0024.

Matrix spikes: A matrix spike and matrix spike duplicate are prepared by adding a known concentration of working standard to a sample prior to distillation and treating like a sample from that point forward. Matrix spikes are used to evaluate the efficiency of the distillation and accuracy of the analysis.

Acceptance criteria: The percent recovery of the matrix spike and matrix spike duplicate must fall between 75 and 125% and the difference between the recoveries must not exceed 25%.

Corrective actions: There are 6 possible combinations possible when comparing the MS/MSD pair to the above listed acceptance criteria.

The 6 combinations and the corresponding corrective actions are listed below.

Both recoveries are between 75 and 125%, and the difference is less than or equal to 25%. No corrective action.

Both recoveries are between 75 and 125%, but the difference is greater than 25%. All samples are flagged with **S1**.

Recovery for one is between 75 and 125%, one is outside this range, and the difference is less than or equal to 25%. All samples are flagged with **S2**.

Recovery for one is between 75 and 125%, one is outside this range, and the difference is greater than 25%. All samples are flagged with **S3**.

Both recoveries are outside acceptable range and the difference is greater than 25%. All samples are distilled and analyzed again with resulting values flagged as **R**.

Both recoveries are outside acceptable range but the difference is less than or equal to 25%. All samples are flagged **M**.

The following information must be recorded in the methyl mercury run sheet.

Date of analysis.

Type and date prepared standards used.

Initials of analysts.

Identification of reaction vessel contents, **From Bottle** number, and sample trap identification for each analysis performed.

Comments pertaining to special samples run, problem samples, corrective actions taken, and results of any calculations performed to ensure acceptance criteria are being met.

Shutdown:

After all samples and standards have been run, thoroughly rinse the bubblers and sparging stoppers with reagent water. Fill the bubblers completely with reagent water. Replace the sparging stopper into the bubbler with the four way valve in the open position to allow the frit to fill with water. When the frit is filled, turn the four-way valve to the closed position. Store the bubbler in the laminar flow hood.

Shut the Ar flow if neither of the total mercury analyzers are being used .

Exit Chromera.

Turn off the plasma and exit Elan. **Do not save changes** to the method file when prompted. Turn the recirculator off.

Create a new folder in the **old** folder in the Chromera Report folder. The naming convention is Mxxxxxx, where xxxxxx represents the six digit date MMDDYY. Cut all of

the reports from the top level of the **Chromera Report** folder (except the **old** folder) and paste them into the new folder within the **old** folder.

Log off HG1.

Reporting of results:

Reporting units: Methyl mercury in ng/L as Hg.

Reporting levels and significant figures:

Report to the nearest 0.01 ng/L for values less than 10 ng/L.

Report to three significant figures for values exceeding 10 ng/L.

Data transfer: After the data has been verified in the EXCEL spread sheet it may be transferred to the customer via e-mail, hard copy, or the internet.

Archiving: All raw data produced in the laboratory is archived in a filing cabinet located in the laboratory manager's office. Hard copies of EXCEL spreadsheets and data reports are archived with raw data. All electronic data is archived on the laboratory manager's computer, which is backed up to tape daily.

References:

Method source:

Horvat, M., Liang, L., Bloom, N.S. 1993, Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II. Water. Analytica Chimica Acta. 282: 153-168

Olson, M.L. Cleckner, L.B., Hurley, J.P., Krabbenhoft, D.P., Heelan, T.W. 1997, Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades. Fresenius Journal Analytical Chemistry. 358: 392-396

U.S. Environmental Protection Agency, 2007, Elemental and speciated isotope dilution mass spectrometry. Method 6800 (Revision 0). 47 pp.

Brooks Rand Merx Procedurefor Automated Methyl:

The procedure for conducting an analysis using the Brooks Rand Merx system instead of bubblers and Carbotraps is very similar. The Merx system consists of three modules: an autosampler, a purge and trap module, and a gas chromatograph/pyrolysis module. The system is accessed through the Mercury Guru software. The Elan software is still used to operate the ICP-MS and the Chromera software is still used to process the chromatograms. Because the Merx goes through a trap clean burning at the beginning of each run, a separate Chromera Method file is not needed for clean burns. However, Chromera report files are generated by the clean burns. Therefore, the sample ID number of the Chromera report will be three higher than the corresponding autosampler vial location number. See the Merx SOP for a detailed discussion of the various components, keeping in mind that the detector has been replaced with the ICP-MS.

8	**7**	**6**	**5**	**4**	**3**	**2**	**1**
16	**15**	**14**	**13**	**12**	**11**	**10**	**9**
24	**23**	**22**	**21**	**20**	**19**	**18**	**17**

32	**31**	**30**	**29**	**28**	**27**	**26**	**25**
40	**39**	**38**	**37**	**36**	**35**	**34**	**33**
48	**47**	**46**	**45**	**44**	**43**	**42**	**41**

56	**55**	**54**	**53**	**52**	**51**	**50**	**49**
64	**63**	**62**	**61**	**60**	**59**	**58**	**57**
72	**71**	**70**	**69**	**68**	**67**	**66**	**65**

The autosampler vial location numbers begin at the upper right corner. Each rack consists of three rows of eight. Three racks can be loaded simultaneously. The following run sheet displays a typical run configuration, consisting of 30 samples (SAM), four distillation blanks (DB), three sets of matrix spike/matrix spike duplicates (MS/MSD), eight ethylation blanks (EB), six check standards (CHK), five mass bias standards (STD), and five ID concentration standards (ID). The vials are prepared by adding approximately 40 ml of sample distillate, 0.2 ml sodium acetate buffer and 0.05 ml NaTEB. Each vial is brought to full volume with the addition of reagent water and capped securely. There should be no bubbles in the vial after it is capped. Because a typical run will consist of 72 vials (including eight ethylation blanks in either positions 1-8, which are used to purge the system, and are not recorded in the run sheet or the analysis spreadsheet), it is strongly recommended that positions 33, 41, 49, 57 and 65 be used for ongoing blanks and positions 32, 40, 48, 56, 64 and 72 be used for check standards.

Date: _____ ID Std: _____ Std: _____ Initials: _____

ID	Rack	Sample ID	To #	Comment
12	9	EB		
13	10	EB		
14	11	EB		
15	12	STD		100
16	13	STD		50
17	14	STD		25
18	15	STD		10
19	16	STD		5
20	17	ID		25 + 25
21	18	ID		25 + 25
22	19	ID		25 + 25
23	20	ID		25 + 25
24	21	ID		25 + 25
25	22	DB 1		
26	23	DB 2		
27	24	DB 3		
28	25	DB 4		
29	26	SAM		
30	27	SAM		
31	28	SAM		
32	29	SAM		
33	30	SAM		
34	31	SAM		
35	32	CHK		10 + 25
36	33	EB		
37	34	SAM		
38	35	SAM		
39	36	SAM		
40	37	SAM		MS
41	38	SAM		MSD
42	39	SAM		
43	40	CHK		50 + 25

ID	Rack	Sample ID	To #	Comment
44	41	EB		
45	42	SAM		
46	43	SAM		
47	44	SAM		
48	45	SAM		
49	46	SAM		
50	47	SAM		
51	48	CHK		25 + 25
52	49	EB		
53	50	SAM		
54	51	SAM		MS
55	52	SAM		MSD
56	53	SAM		
57	54	SAM		
58	55	SAM		
59	56	CHK		100 + 25
60	57	EB		
61	58	SAM		
62	59	SAM		
63	60	SAM		
64	61	SAM		
65	62	SAM		
66	63	SAM		
67	64	CHK		50 + 25
68	65	EB		
69	66	SAM		
70	67	SAM		
71	68	SAM		MS
72	69	SAM		MSD
73	70	SAM		
74	71	SAM		
75	72	CHK		5 + 25